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SYNTHESIS AND REACTIVITY OF
(BIS(TRIMETHYLSILYL)METHYLENE)(MESITYL)PHOSPHINE(U)
TEXAS CHRISTIAN UNIV FORT WORTH DEPT OF CHEMISTRY

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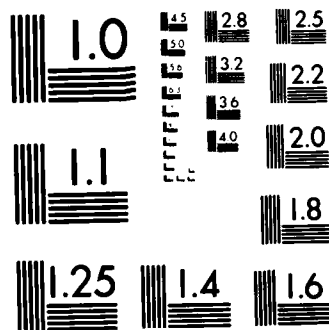
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Synthesis and Reactivity of [Bis(trimethylsilyl)methylene]
(mesityl)phosphine

by

Z.-M. Xie, P. Wisian-Neilson and R. H. Neilson

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Synthesis and Reactivity of
[Bis(trimethylsilyl)methylene](mesityl)phosphine¹

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Abstract

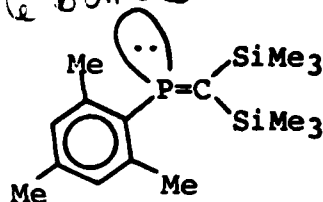
The title compound $\text{MesP}=\text{C}(\text{SiMe}_3)_2$ (2) is prepared by the dehydrohalogenation reaction of the chlorophosphine $\text{MesP}(\text{Cl})\text{CH}(\text{SiMe}_3)_2$ (1) with DBU. The (methylene)phosphine 2 readily undergoes addition and oxidation reactions characteristic of a polar P=C double bond. Addition of methanol, for example, yields the methoxyphosphine $\text{MesP}(\text{OMe})\text{CH}(\text{SiMe}_3)_2$ (4) while treatment with MeLi produces the reactive, ambident anion $[\text{MesP}(\text{Me})\text{C}(\text{SiMe}_3)_2]^-$ (5). Reactions of 5 with MeOH and MeI afford the methylphosphine $\text{MesP}(\text{Me})\text{CH}(\text{SiMe}_3)_2$ (6) and the stable ylide $\text{MesPMe}_2=\text{C}(\text{SiMe}_3)_2$ (7), respectively. Compound 6 is also obtained from 1 (by reaction with MeLi) or from the P-H phosphine $\text{MesP}(\text{H})\text{CH}(\text{SiMe}_3)_2$ (3, prepared via 1 plus LiAlH_4) by treatment of its MeI salt with *n*-BuLi. A trisilylated imino(methylene)-phosphorane $\text{MesP}(=\text{NSiMe}_3)=\text{C}(\text{SiMe}_3)_2$ (8), a methylene(thioxo)-phosphorane $\text{MesP}(=\text{S})=\text{C}(\text{SiMe}_3)_2$ (9), and a thiaphosphirane $\text{MesP}(\overline{=\text{S}})-\text{S}-\text{C}(\text{SiMe}_3)_2$ (10) result from the oxidation reactions of 2 with either Me_3SiN_3 or elemental sulfur. Compound 10 is smoothly desulfurized by *n*-Bu₃P to yield 9. Proton, ¹³C, and ³¹P NMR data are reported for the new compounds and the chemistry of 2 is contrasted and compared with that of other (methylene)-phosphines such as $\text{MesP}=\text{CPh}_2$.

RP-C P Double bond

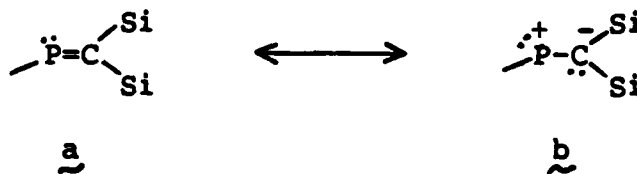
Introduction

In two recent papers^{2,3}, we have described the synthesis and characterization of a series of P-mesityl substituted phosphorus compounds containing Si-N-P and/or Si-C-P linkages. These systems are of interest, in part, as precursors to new types of low-coordinate phosphorus compounds including (methylene)phosphines, $RP=CR_2$ ⁴, and imino(methylene)phosphoranes, $RP(=NR)=CR_2$ ⁵. As an extension of these studies, we report here the synthesis and some derivative reactions of [bis(trimethylsilyl)methylene](mesityl)phosphine.⁶

RP(-NR)-CR₂ double bonds



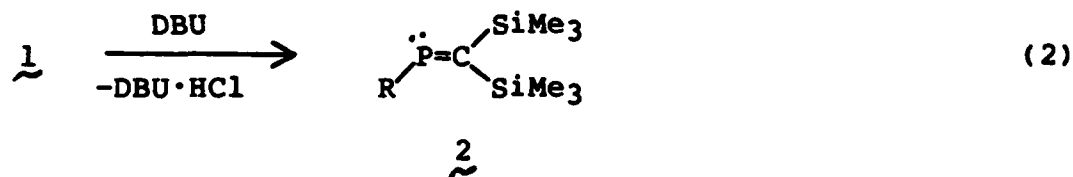
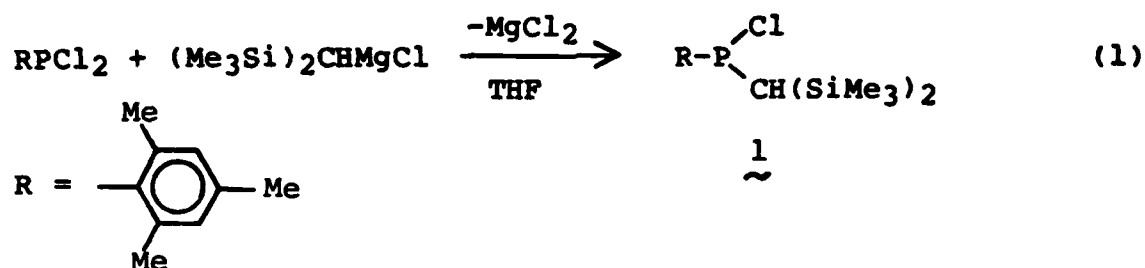
As well as imparting kinetic stability to such a compound, the silyl groups on carbon also serve to modify the reactivity of the P=C double bond. The π -acceptor ability of silicon should accentuate the polarity of the bond by stabilizing the dipolar form (b). Thus, the chemistry of this (disilylmethylene)phosphine



may be expected to be quite different, for example, from that of the diphenylmethylene analog, $MesP=CPh_2$, as prepared and studied by Bickelhaupt and coworkers.⁷

Results and Discussion

Synthesis of the (methylene)phosphine. The new [bis(trimethylsilyl)methylene]phosphine 2 was prepared by the dehydrohalogenation of the appropriate chlorophosphine 1 (eq 1) using DBU (in 50% molar excess) as the HCl acceptor (eq 2).



Similar dehydrohalogenation procedures have been used in our laboratory^{5a} and elsewhere^{4,7} for the synthesis of various P=C derivatives. Alternatively, the close analogs $\text{RP}=\text{C}(\text{SiMe}_3)_2$ (R = Ph, *t*-Bu) were obtained via the thermolysis of [tris(trimethylsilyl)methyl]phosphines, $\text{RP}(\text{Cl})\text{C}(\text{SiMe}_3)_3$.⁸ The convenient synthesis of the reagent $(\text{Me}_3\text{Si})_2\text{CHCl}$ ⁹, however, makes the dehydrohalogenation process a much simpler, higher-yield route to the P=C system.

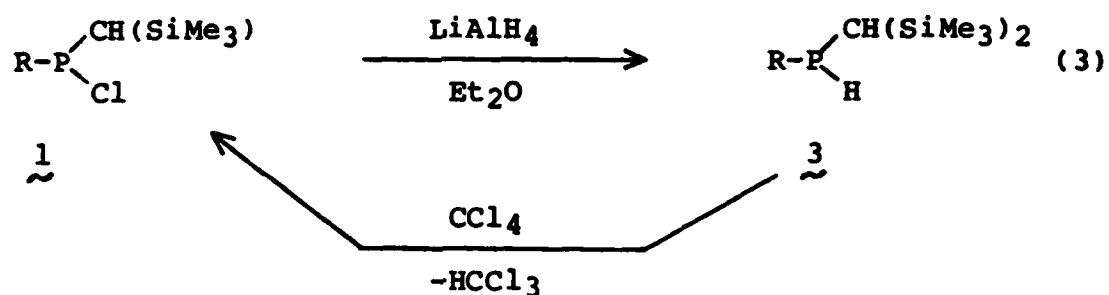
The (methylene)phosphine 2 was isolated by fractional distillation in ca. 65-70% yield as an air-sensitive yellow

liquid which crystallized on standing. It was fully characterized by NMR spectroscopy (^1H , ^{13}C , and ^{31}P) and by elemental analysis (Tables I and II). Noteworthy features of the NMR spectra of 2 include the ^{31}P and ^{13}C chemical shifts of the P=C moiety which confirm sp^2 hybridization at these centers. In comparison to the related diphenylmethylene derivative⁷, the ^{31}P NMR signal is shifted to lower field by ca. 150 ppm. This is consistent with a more highly polarized P=C double bond having a greater degree of positive charge on phosphorus. Similar low-field shifts are known for other C-silylated (methylene)-phosphines^{5a,8} and for the isoelectronic disilylamino substituted phosphonium ions, $\text{R}-\overset{+}{\text{P}}-\text{N}(\text{SiMe}_3)_2$.¹⁰

The NMR spectral data also shed light on some of the stereochemical features of 2. In spite of the enhanced polarity, the degree of π -bonding is still sufficient to cause restricted rotation about the P=C double bond. This is clearly shown by the observation of nonequivalent Me_3Si groups in both the ^1H and ^{13}C NMR spectra (Table I). Based on other work,^{5a,8,11,12} the signals having the larger couplings (J_{PH} and J_{PC}) to phosphorus can be reasonably assigned to the Me_3Si group that is in a cis relationship to the phosphorus lone pair (i.e., the E position in 2). Rotation about the mesityl-P bond, on the other hand, is rapid on the NMR time scale as indicated by the simplicity of the signal patterns of the mesityl group in the ^{13}C spectrum.

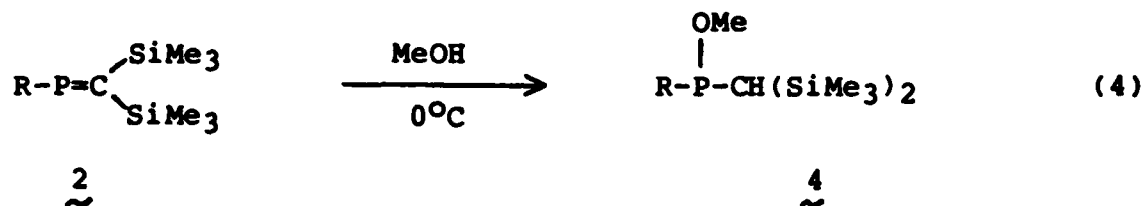
In contrast to the (methylene)phosphine 2, the chlorophosphine precursor 1 could not be completely purified and

characterized due, in part, to its thermal instability. Nevertheless, 1 was routinely prepared (eq 1) in synthetically useful form as a viscous, orange liquid. It was characterized by ^1H and ^{31}P NMR spectroscopy in addition to its derivative chemistry. The reaction with LiAlH_4 (eq 3), for example, afforded the distillable P-H derivative 3 which, upon treatment with CCl_4 , was reconverted to 1.



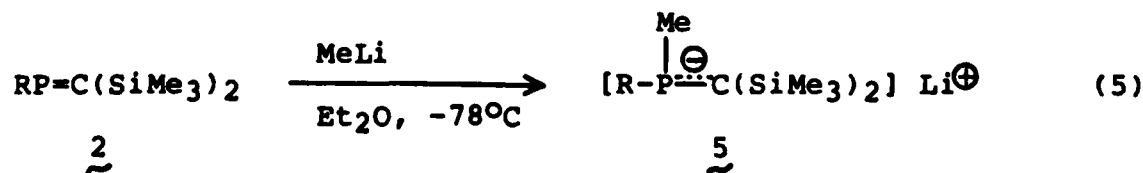
Reactions of the (methylene)phosphine. Two general modes of reactivity of 2 were investigated: (1) addition of polar reagents to the P=C double bond, and (2) oxidation of the phosphorus center to yield stable 3-coordinate P(V) derivatives. In both cases, the silyl substituents on carbon help to greatly simplify the chemistry, first, by increasing the polarity of the double bond and, second, by kinetically stabilizing the products of many reactions.

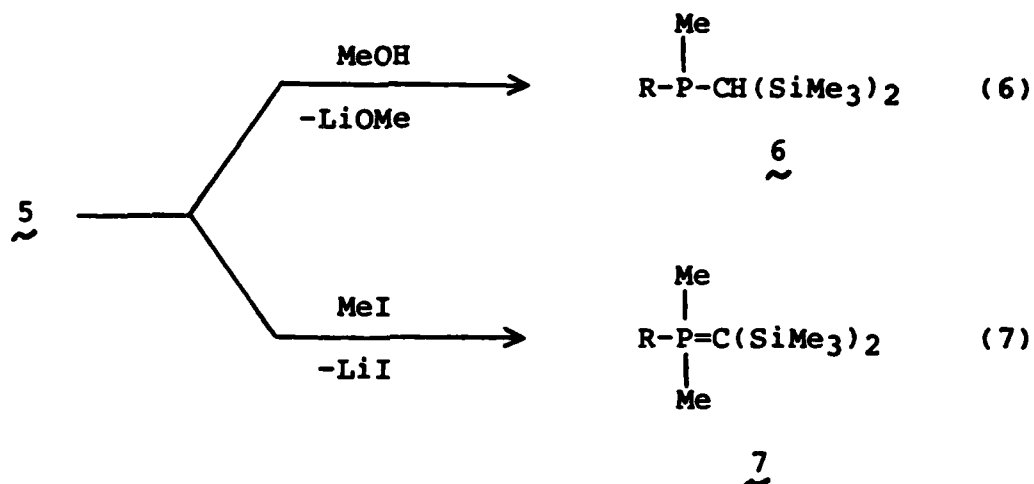
The first of these points is well illustrated by the addition of methanol to 2 which occurs rapidly and quantitatively at 0°C (eq 4). In contrast, the diphenyl analog $\text{MesP}=\text{CPh}_2$ is



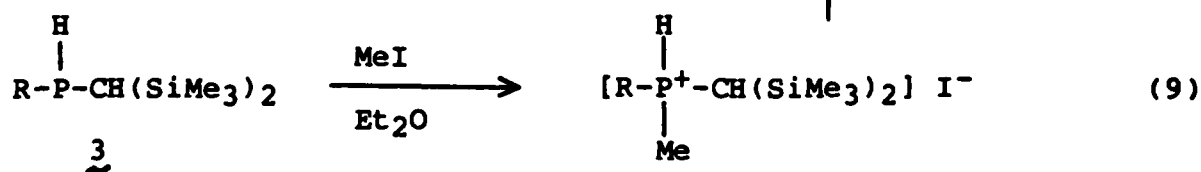
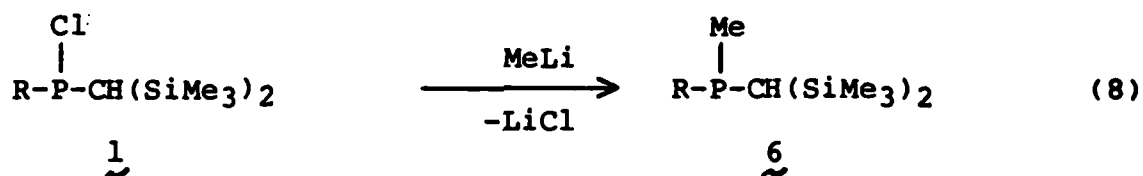
completely unreactive toward EtOH under similar conditions.^{7b} Formation of the methoxyphosphine 4 clearly shows the polarity of the P=C double bond and it parallels similar reactivity of some other (methylene)phosphines.^{5a,12} The polarity can, however, be reversed by introducing π -donor substituents on carbon as demonstrated by recent MO calculations.^{7c} Indeed, Becker¹³ has obtained P-H products from the methanolysis of C-NMe₂ substituted (methylene)phosphines. The relatively high field ³¹P shifts (ca. δ 10-90) of these latter compounds are also consistent with the reversed polarity P(δ^-)-C(δ^+) of their P=C double bonds.

A synthetically more useful reaction of the (methylene)phosphine 2 occurs with alkyllithium reagents. For example, treatment of 2 with one equivalent of MeLi in Et₂O at -78°C yields a solution of the reactive anion 5 (eq 5). Although it was not isolated, 5 appears to be stable in solution at room temperature (δ ³¹P = -20.1). The ambident nature of anion 5 was demonstrated by its reactions with MeOH (eq 6) and MeI (eq 7)





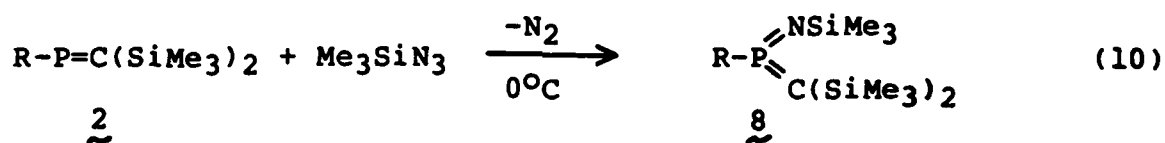
which gave the carbon- (6) and phosphorus-bonded (7) products, respectively. The identity of the methylphosphine 6 was confirmed by its preparation via two independent routes (eqs 8 and 9) as well as NMR spectroscopy (Table I) and elemental analysis. The assignment of the ylide structure of 7, a stable



distillable liquid, was verified by NMR spectral data with two points being particularly diagnostic: (1) the equivalence of the P-methyl and C-silyl groups in both ^1H and ^{13}C spectra, and (2) the dramatic upfield ^{13}C shift ($\delta -1.65$) of the ylidic carbon.

The formation of anion 5 and its subsequent reactions provide good evidence that the reaction of (methylene)phosphines with organometallic reagents occurs by nucleophilic addition to the P=C double bond.¹⁴ Other reactions of this type have involved 2-coordinate phosphines bearing $(\text{Me}_3\text{Si})_2\text{N}^{15}$ or Cl^4 groups on phosphorus in which nucleophilic substitution occurs. The first-formed anionic intermediates, analogous to 5, however, could not be detected in such cases.

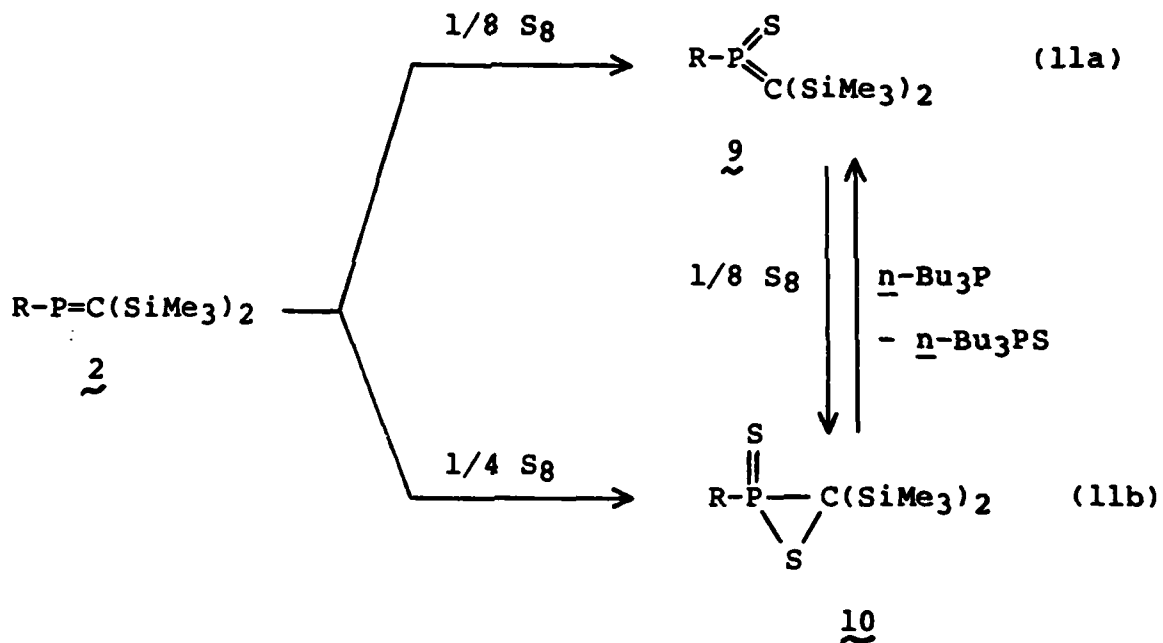
The second general type of reaction, i.e. oxidation to the 3-coordinate P(V) state is illustrated by the reaction of 2 with trimethylsilylazide (eq 10) which gave the iminophosphorane 8. Compound 8, a thermally stable, distillable product, was readily



characterized by its ^{31}P ($\delta 120.0$) and ^{13}C ($\delta 75.12$, $J_{\text{PC}} = 81.8$ Hz) NMR spectra and elemental analysis. The NMR data preclude the possibility of the isomeric cyclic structure, $\overline{\text{RPN(SiMe}_3)\text{C(SiMe}_3)_2}$, for 8 since such strained ring systems normally have very high field ^{31}P shifts.^{5c} The observation of three distinct Me_3Si signals in both the ^1H and ^{13}C spectra show

that there is restricted rotation, as in 2, about the P=C double bond. The stabilizing influence of the Me₃Si groups is clearly evident here since the related disilylated compound MesP(=NSiMe₃)=CHSiMe₃³ is stable for only a few hours at room temperature.

The oxidation of (methylene)phosphine 2 by elemental sulfur (eq 11) was also studied as part of this project.⁶ Treatment of 2 with one equivalent of sulfur resulted in an inseparable



mixture of the methylene(thio)phosphorane 9, the thiaphosphirane 10, and starting material 2. Addition of a second equivalent of sulfur afforded complete conversion of the mixture to 10. A pure sample of 9 was then obtained by the desulfurization reaction of 10 with n-Bu₃P. Both 9 and 10 are fully-characterized, crystalline solids that have been studied by

X-ray crystallography.⁶ The methylene(thioxo)phosphorane 9 represents a stable analog to the intermediate proposed by Bickelhaupt^{7b} for the oxidation of $\text{MesP}=\text{CPh}_2$ by sulfur. Earlier, Niecke and Wildbrecht¹⁶ had reported stable, but non-crystalline, analogs of both 9 and 10 from the sulfur oxidation of $(\text{Me}_3\text{Si})_2\text{NP}=\text{CHSiMe}_3$.

The ^{13}C and ^{31}P NMR spectra of 9 (Table I) show the expected low-field signals for the sp^2 hybridized carbon and phosphorus atoms. The trigonal planar geometry at both centers and the short $\text{P}=\overset{\text{O}}{\text{C}}$ double bond (1.65 Å) were confirmed by the X-ray structural analysis.⁶ Moreover, the two widely separated signals for the Me_3Si groups in the ^{13}C and ^1H NMR spectra of 9 indicate that, even in solution, the Me_3Si groups are locked into different environments by the restricted rotation about the $\text{P}=\text{C}$ double bond.

In the 3-membered ring system 10, both the $\text{P}-\text{C}$ carbon and phosphorus resonances occur at significantly higher field than in 9, reflecting the hybridization change.⁶ The value of J_{PC} (8.6 Hz) in 10 is exceptionally low in comparison to the already small coupling constant ($J_{\text{PC}} = 28.2 \text{ Hz}$)¹⁶ in $(\text{Me}_3\text{Si})_2\text{NP}(\text{=S})-\text{S}-\text{CHSiMe}_3$. The additional ring strain in 10 caused by the two bulky Me_3Si substituents on the ring is probably responsible for this difference. The steric congestion in 10 is also apparent in the ^{13}C NMR spectrum which shows a doubling of all of the mesityl signals due to hindered rotation about the mesityl-P bond.

As a final point of interest, the facile conversion of 9 to 10 by the second equivalent of sulfur may be viewed as the formation of a π -complex between the P=C bond of 9 and the sulfur atom. The extension of this concept to the possible preparation of η^2 -complexes of 9, and the related compound 8, with transition metals is under investigation.

Experimental Section

Materials and General Procedures. The following reagents were obtained from commercial sources and used without purification: LiAlH_4 , MeLi, *n*-BuLi, MeI, Me_3SiN_3 , sulfur, *n*-Bu₃P, and MeOH. Tetrahydrofuran (THF) was distilled from Na/benzophenone immediately prior to use. Other solvents were distilled from CaH_2 . Moisture was removed from DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) as the azeotrope with benzene. The DBU was then distilled (bp 80-83°/0.6mm) and stored over molecular sieves. The published procedure⁹ was used to prepare $(\text{Me}_3\text{Si})_2\text{CHCl}$ on a 0.5-0.7 mole scale from Me_3SiCl , CH_2Cl_2 , and *n*-BuLi. Mesityldichlorophosphine, MesPCl_2 , was prepared as before² from PCl_3 and MesMgBr . When prepared in this manner, MesPCl_2 usually contains small amounts (ca. 10-20%) of the P-Br analogs due to halide exchange. This does not interfere with its subsequent derivative reactions. Proton NMR spectra were recorded on a Varian EM-390 spectrometer; ^{13}C and ^{31}P NMR, both with ^1H decoupling, were obtained in the FT mode on a JEOL FX-60 instrument. Elemental analyses were performed by Schwarzkopf

Microanalytical Laboratory, Woodside, N.Y. All reactions and other manipulations were carried out under an atmosphere of dry nitrogen and/or under vacuum. The procedures described herein are typical of those used for the preparation of the new compounds in this study.

[Bis(trimethylsilyl)methyl]magnesium chloride. A few mL of a solution of $(\text{Me}_3\text{Si})_2\text{CHCl}$ (9.73 g, 0.050 mol) in THF (25 mL) was added to a preheated flask (ca. 90°C) containing Mg turnings (1.15 g, 0.050 mol). After the reaction started, the remaining solution was added continuously at a rate sufficient to maintain reflux. The mixture was then refluxed for 3 h (or stirred overnight at room temperature), cooled, and diluted with THF (25 mL) to afford an approximately 1 M solution of the Grignard reagent. When the use of larger quantities (ca. 0.1-0.5 mol) was required, the following procedure¹⁷ was found to be more convenient. A 500 mL round-bottom flask was equipped with a magnetic stir bar, an addition funnel, and a reflux condenser. The flask was charged with Mg turnings (6.60 g, 0.272 mol) and THF (70 mL). The Mg was activated with 1,2-dibromoethane (2.0 mL, 0.023 mol). When the evolution of ethylene had subsided, a solution of $(\text{Me}_3\text{Si})_2\text{CHCl}$ (46.3 g, 0.238 mol) in THF (170 mL) was added dropwise at a rate sufficient to maintain steady reflux of the THF. After the addition was complete, the solution was allowed to stir for ca. 2 h. The mixture was usually then transferred via a double-ended syringe needle to an addition funnel for use in subsequent reactions.

[Bis(trimethylsilyl)methyl](chloro)(mesityl)phosphine 1. A solution of $(\text{Me}_3\text{Si})_2\text{CHMgCl}$ (50 mL, ca. 1 M in THF) was added dropwise to a stirred solution of MesPCl_2 (11.0 g, 0.050 mol) in THF (50 mL) at 0°C . The mixture was stirred overnight at room temperature, THF was removed under reduced pressure, and hexane (100 mL) was added. After filtration and solvent removal, the viscous orange liquid which remained was identified as 1 by ^1H and ^{31}P NMR spectral data (Table I). Attempted purification by distillation resulted in decomposition to unidentified products. The ^{31}P spectrum of 1 indicates the presence of an impurity (ca. 10%), believed to be the bromophosphine analog ($\delta^{31}\text{P} = 110.5$) due to bromide contamination in the MesPCl_2 . Nevertheless, this crude product 1 gave satisfactory yields of pure derivatives 2 and 3.

[Bis(trimethylsilyl)methylene](mesityl)phosphine 2. A stirred solution of 1 (27.6 g, 0.080 mol), prepared as above, in Et_2O (200 mL) was treated with DBU (19.4 mL, 0.13 mol) at room temperature. A white solid formed while the mixture was stirred overnight. The Et_2O was removed and hexane (200 mL) was added. After filtration and solvent removal, fractional distillation through a 10-cm Vigreux column afforded 2 as a yellow liquid which solidified upon standing (mp $32\text{--}33^\circ\text{C}$).

[Bis(trimethylsilyl)methyl](mesityl)phosphine 3. A solution of LiAlH_4 (30 mL, 1.0 M in Et_2O , 0.12 mol hydride) was added dropwise to a stirred solution of 1 (34.5 g, 0.10 mol) in Et_2O (100 mL) at 0°C . After being stirred overnight at room

temperature, the mixture was filtered and the solvent was removed under vacuum. Distillation afforded 3 as a colorless liquid.

Reaction of 3 with CCl₄. Carbon tetrachloride (1.5 g) was added to a solution of 3 (3.0 g) in CH₂Cl₂ (15 mL) at 0°C. The mixture was warmed to room temperature and stirred for 72 h. Solvent removal left 1 as a viscous liquid which was spectroscopically identical to that prepared as described above.

[Bis(trimethylsilyl)methyl](mesityl)(methoxy)phosphine 4. Anhydrous methanol (0.54 g, 17 mmol) was added at 0°C to a neat sample of 2 (5.4 g, 17 mmol). After stirring 4 h at room temperature, distillation gave 4 as a colorless liquid.

[Bis(trimethylsilyl)methyl](mesityl)(methyl)phosphine 6.
 (a) From anion 5. Methylolithium (24 mL, 1.4 M in Et₂O, 34 mmol) was added via syringe to a stirred solution of (methylene)-phosphine 2 (10.5 g, 34 mmol) in Et₂O (70 mL) at -78°C. The mixture was warmed to room temperature and was stirred for 30 min. Quantitative formation of the anion 5 (δ ³¹P = -20.1) was shown by ³¹P NMR. The mixture was recooled to -78°C and MeOH (1.1 g, 34 mmol) was added. The mixture was warmed to room temperature, stirred overnight, and freed of solvent. Following addition of hexane (100 mL), filtration, and solvent removal, distillation afforded 6 as a colorless liquid. (b) From chlorophosphine 1. In a 10-mm NMR tube, 1 (ca. 1 mmol in 1 mL of Et₂O) was treated with an equivalent of MeLi in Et₂O. Complete conversion to 6 was indicated by ³¹P and ¹H NMR spectroscopy (the ¹H NMR signals of 6 were not obscured by those of the Et₂O solvent). (c) From P-H

phosphine 3. In a similar manner, 3 was allowed to react with one equivalent of MeI in Et₂O solution. Formation of the intermediate phosphonium salt [MesP⁺(Me)(H)CH(SiMe₃)₂] I⁻ was shown by ³¹P NMR (δ -14.15, J_{PH} = 476 Hz). Addition of an equimolar quantity of n-BuLi resulted in an exothermic reaction with complete conversion to 6. Presumably, less reactive bases could also be used to dehydrohalogenate the phosphonium salt.

[Bis(trimethylsilyl)methylene](dimethyl)(mesityl)phosphorane 7. Iodomethane (1.4 g, 10 mmol) was added via syringe to a stirred solution of anion 5 (8.4 mmol) in Et₂O (15 mL) at -78°C. By using the same workup procedure as described above for 6, compound 7 was isolated by distillation as a colorless liquid. The product reacted with CDCl₃ to give a mixture of two products (δ ³¹P = 23.3 and 20.0) which were not identified. The ¹³C and ³¹P NMR spectra of 7 were, therefore, recorded using CD₂Cl₂ as the solvent.

[Bis(trimethylsilyl)methylene](mesityl)(trimethylsilylimino)-phosphorane 8. A neat sample of compound 2 (12.0 g, 39 mmol) was treated at 0°C with an excess of Me₃SiN₃ (7.5 g, 65 mmol). An exothermic reaction occurred with evolution of a gas, presumably N₂. Distillation afforded 8 as a colorless liquid that solidified on standing (mp 49-50°C).

[Bis(trimethylsilyl)methylene](mesityl)(thioxo)phosphorane 9. Tri-n-butylphosphine (2.1 mL, 8.4 mmol) was added via syringe to a stirred solution of 10 (3.12 g, 8.4 mmol, prepared as described below) in benzene (10 mL) at 0°C. After warming to room

temperature, ^{31}P NMR showed the formation of 9 and $n\text{-Bu}_3\text{P}=\text{S}$ (δ 46.50). The solvent was removed and distillation through a short path column gave a yellow liquid which solidified in the receiving flask and the condenser. The solids were combined and recrystallized from hexane to give 9 as white crystals (mp 95-100°C).

Thiaphosphirane 10. Sulfur (0.9 g, 28 mmol) was added to a stirred solution of 2 (4.4 g, 14 mmol) in benzene (80 mL) at room temperature. After stirring overnight, the solvent was removed and the solid product was recrystallized from hexane (25 mL) to give 10 as white crystals (mp 139-141°C). Preliminary experiments showed that the reaction of 2 with one equivalent of sulfur gave an inseparable mixture of 9, 10, and unreacted 2.

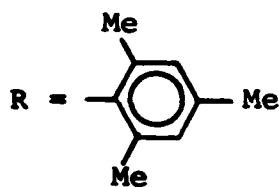
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Table I. NMR Spectroscopic Data^a for Mesityl(R)-Phosphorus Compounds



compd	signal	¹ H NMR		¹³ C NMR		³¹ P NMR
		δ	J _{PH}	δ	J _{PC}	δ
$\begin{array}{l} \text{Cl} \\ \\ \text{R}-\text{P} \\ \\ \text{CH}(\text{SiMe}_3)_2 \end{array}$ <p>1</p>	Me ₃ Si	-0.08				104.9
		0.32	1.5			
	CH	2.27	12.0			
	o-Me	2.67				
	p-Me	2.26				
	C ₆ H ₂	6.90	3.2			
$\text{R}-\text{P}=\text{C}(\text{SiMe}_3)_2$ <p>2</p>	Me ₃ Si	-0.20		1.76	3.0	381.0
		0.27	1.9	2.35	17.7	
	P=C			204.18	86.9	
	o-Me	2.19		21.78	8.2	
	p-Me	2.19		21.11		
	C ₆ H ₂	6.79				
	C ₁			143.12	64.1	
	C _{2,6}			138.23	1.2	
	C _{3,5}			128.36		
	C ₄			137.82		

Table I. continued

compd	signal	¹ H NMR		¹³ C NMR		³¹ P NMR	
		δ	J _{PH}	δ	J _{PC}	δ	
$\begin{array}{c} \text{H} \\ \diagup \\ \text{R}-\text{P} \\ \diagdown \\ \text{CH}(\text{SiMe}_3)_2 \end{array}$ <p>3</p>	Me ₃ Si	0.07		0.73		-88.56	
		0.10		1.03	4.3		
	CH	0.78	0.0 _b	5.68	37.2		
	PH	4.67	218 _b				
	o-Me	2.53		23.02	12.2		
	p-Me	2.12		20.83			
	C ₆ H ₂	7.00	2.3				
	C ₁			131.63	23.8		
	C _{2,6}			142.13	13.4		
	C _{3,5}			128.93	2.4		
	C ₄			137.70			
	$\begin{array}{c} \text{OMe} \\ \diagup \\ \text{R}-\text{P} \\ \diagdown \\ \text{CH}(\text{SiMe}_3)_2 \end{array}$ <p>4</p>	Me ₃ Si	-0.11		1.32	4.9	139.9
			0.24		2.39	4.9	
		CH	1.84	5.3	19.90	51.9	
OMe		3.59	15.1	54.96	22.6		
o-Me		2.62		21.91	20.1		
p-Me		2.23		20.99			
C ₆ H ₂		6.83	1.2				
C ₁				134.94	47.3		
C _{2,6}				143.00	17.7		
C _{3,5}				129.80	3.0		
C ₄				139.25	1.2		

Table I. continued

compd	signal	¹ H NMR		¹³ C NMR		³¹ P NMR	
		δ	J _{PH}	δ	J _{PC}	δ	
$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{R}-\text{P} \\ \diagup \\ \text{CH}(\text{SiMe}_3)_2 \end{array}$ <p>6</p>	Me ₃ Si	-0.17		1.40	4.3	-42.9	
		0.19		2.53	5.5		
	CH	1.26	3.1	15.02	19.5		
	PMe	1.43	6.6	11.95	53.3		
	o-Me	2.53		23.29	20.1		
	p-Me	2.19		20.83			
	C ₆ H ₂	6.81	2.4				
	C ₁			135.04	25.0		
	C _{2,6}			143.45	15.3		
	C _{3,5}			129.71	3.7		
	C ₄			138.31	1.2		
	$\begin{array}{c} \text{Me} \\ \\ \text{R}-\text{P}=\text{C}(\text{SiMe}_3)_2 \\ \\ \text{Me} \end{array}$ <p>7c</p>	Me ₃ Si	-0.07		5.98	4.0	6.6
		PMe ₂	1.80	11.5	26.26	54.7	
P=C				-1.65	61.5		
o-Me		2.58		24.76	2.0		
p-Me		2.21		21.05			
C ₆ H ₂		6.87	3.3				
C ₁				131.87	81.1		
C _{2,6}				141.93	8.8		
C _{3,5}				131.67	10.7		
C ₄				140.18	2.9		

Table I. continued

compd	signal	¹ H NMR		¹³ C NMR		³¹ P NMR	
		δ	J _{PH}	δ	J _{PC}	δ	
$\begin{array}{c} \text{NSiMe}_3 \\ \text{R}-\text{P}=\text{C}(\text{SiMe}_3)_2 \\ \sim \\ \text{8} \end{array}$	<u>Me₃SiC</u>	-0.21		2.56	1.2	120.0	
		0.28		2.96	2.4		
	Me ₃ SiN	-0.25		1.96	4.3		
	P=C			75.12	81.8		
	o-Me	2.52	1.8	22.51	6.7		
	p-Me	2.04		21.44			
	C ₆ H ₂	6.91	2.8				
	C ₁			136.66	80.0		
	C _{2,6}			137.84	9.2		
	C _{3,5}			128.18	10.4		
	C ₄			140.97	3.0		
	$\begin{array}{c} \text{S} \\ \text{R}-\text{P}=\text{C}(\text{SiMe}_3)_2 \\ \sim \\ \text{9} \end{array}$	Me ₃ Si	-0.22		2.11		190.9
			0.39		2.56		
P=C				126.00	34.2		
o-Me		2.51	1.5	22.50	7.3		
p-Me		2.23		21.48			
C ₆ H ₂		6.91	4.8				
C ₁				131.74	78.7		
C _{2,6}				137.99	8.5		
C _{3,5}				128.79	11.6		
C ₄				141.78	3.1		

Table I. continued

compd	signal	^1H		^{13}C NMR		^{31}P NMR
		δ	J_{PH}	δ	J_{PC}	δ
$ \begin{array}{c} \text{S} \\ \parallel \\ \text{R}-\text{P}-\text{C}(\text{SiMe}_3)_2 \\ \diagdown \quad \diagup \\ \text{S} \\ \sim 10^{\text{d}} \end{array} $	Me ₃ Si	-0.26		-0.14	3.1	2.60
		0.38		1.66	3.4	
	P-C			26.39	8.6	
	o-Me	2.66	1.5	22.76	4.3	
		2.57	1.1	22.19	5.5	
	p-Me	2.20		21.15	1.2	
	C ₆ H ₂	6.83				
		6.89				
	C ₁			133.09	97.1	
	C _{2,6}			139.08	7.3	
			138.29	12.8		
C _{3,5}			129.91	13.4		
			128.99	14.0		
C ₄			141.58	3.0		

^aChemical shifts downfield from Me₄Si for ^1H and ^{13}C and from H₃PO₄ for ^{31}P spectra; coupling constants in Hz. Solvents: ^1H , CH₂Cl₂; ^{13}C and ^{31}P , CDCl₃ except where noted. ^b $J_{\text{HCPH}} = 7.5$ Hz. ^cSolvent: CD₂Cl₂. ^dHindered rotation about R-P bond.

Table II. Preparative and Analytical Data

Compd	preparative		analytical ^a	
	% yield	bp, °C (mm)	% C	% H
<u>2</u>	66	77-75 (0.01)	61.88 (62.33)	9.68 (9.41)
<u>3</u>	47	89 (0.03)	61.31 (61.91)	9.64 (9.99)
<u>4</u>	87	84-85 (0.03)	59.65 (60.17)	9.75 (9.72)
<u>6</u>	82	92-93 (0.02)	62.32 (62.91)	10.22 (10.25)
<u>7</u>	80	114-115 (0.03)	63.26 (63.85)	10.25 (10.42)
<u>8</u>	80	89-90 (0.02)	57.56 (57.71)	9.67 (9.61)
<u>9</u>	49	90 (0.01)	56.32 (56.42)	8.56 (8.58)
<u>10</u>	70	mp 139-141	51.75 (51.56)	7.98 (7.84)

^aCalculated values in parentheses.

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